



	<b>Experiment title:</b> EXAFS study on the complexation of Am(III) with thiocyanate	<b>Experiment number:</b> 20-01-785
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#### Report:

The complexation of Am(III) with thiocyanate ( $\text{SCN}^-$ ) has been investigated as a function of ligand concentration at room temperature under ambient air conditions at pH 2.0. Additionally, due to generous allocation of beam time, the complexation of Am(III) with sulfate ( $\text{SO}_4^{2-}$ ) has been investigated. A total of six samples of the Am-SCN system, five samples of the Am-SO<sub>4</sub> system, as well as one sample of the Am(III) aquo ion, have been prepared. The concentration of Am(III) was held constant throughout all samples at 1 mmol/L. The concentration of thiocyanate ranged between 1 - 6 mol/L at constant ionic strength with two additional samples at a concentration of 10 mol/L and thiocyanate saturation. The concentration of sulfate ranged between 1 - 500 mmol/L, respectively, whereas the pH was not varied. 200  $\mu\text{L}$  of each sample solution were encapsulated in a type SH23 container and analyzed using EXAFS spectroscopy. EXAFS spectra were recorded at the Am L<sub>III</sub>-edge (18515 eV) in fluorescence mode using the 13-element Ge detector positioned at an angle of 90° to the incoming beam. Analysis of the spectra was performed with the software packages EXAFSPAK [1] and FEFF8.40 [2]. The scattering phases and amplitudes for the thiocyanate and sulfate system were calculated using the crystal structure of  $[\text{Eu}(\text{H}_2\text{O})_5(\text{SCN})_3] \cdot \text{H}_2\text{O}$  [3], in which thiocyanate is in undistorted linear configuration bound to Eu via the nitrogen atom (Eu replaced by Am), and  $\text{Am}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$  [4], respectively. The theoretical model was fit to the raw  $k^3$ -weighted Am L<sub>III</sub>-edge EXAFS spectra.

For the Am(III) sulfate system, sample 2-5 were measured at a good signal/noise ratio. In all cases 9-10 oxygen neighbours are found in the first coordination sphere at an interatomic distance of  $2.48 \pm 0.01 \text{ \AA}$ . Due to the small contribution of the sulfur shell to the overall EXAFS amplitude throughout the whole series (< 10%), no sulfur could be observed in sample 2 featuring the lowest sulfate concentration (1 mmol/L). In contrast to this, sample 3-5 show a continuous increase in impact of sulfur in the second coordination sphere located at an interatomic distance of 3.68-3.79  $\text{Å}$ . These values lie in the same range as the interatomic distance in the crystal structure of  $\text{Am}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$  pointing out the identicalness of the coordination mode of the sulfate ligands towards Am(III) being monodentate through one sulfate oxygen only.

The experimentally determined coordination numbers with respect to sulfur have been compared to the values expected from thermodynamic calculations using stability constants for the formation of  $[\text{AmSO}_4]^+$  and  $[\text{Am}(\text{SO}_4)_2]^-$  tabulated in the NIST database 46.7 ( $\log \beta_1^0 = 3.8$ ,  $\log \beta_2^0 = 5.4$ ) and agree within the experimental error range.

In case of the Am thiocyanate system, data evaluation is still ongoing. While significant forward-scattering in case of reasonably electron-rich linear ligands like thiocyanate was expected, no evidence of this effect could be found. However, Fourier back transformation of the first coordination shell suggests two subshells of similar intensity at very close distance, which suggests coordination of thiocyanate through the nitrogen atom. Hence, further data treatment, e.g. through PCA and wavelet transform procedures, is necessary to achieve consistent data interpretation.

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